

Miniature High Density Scandate Cathodes For Linear Beam Devices

By

Bernard K. Vancil, Ivor Brodie, Arthur Carpenter

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Bernard Vancil

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Summary

The work was an investigation of recent promising results by workers in China on scandate impregnated cathodes. The improvement in dispenser cathode performance due to additions of small quantities of scandium oxide has been known since at least the 1980's. But workers in China have produced breakthrough performance with verified current loadings to 100 A/cm^2 . These results have not been fully reproduced or understood by cathode researchers in this country. Sustained loading of 100 A/cm^2 would be about a ten-fold improvement over existing technology. It would enable significant improvements in vacuum microwave, millimeter wave, and terahertz linear beam sources and amplifiers.

The project concentrated first on verifying the Chinese results. To this end, we obtained scandate cathodes from The Beijing Institute of Technology (BJUT) and tested them in close-spaced diode format and in open-structure pierce gun testers. These latter devices were designed for loadings up to 100 A/cm^2 , and in fact, were tested to over 50 A/cm^2 during the course of the project. The results were excellent and seem to verify the Chinese claims. Close-spaced diode tests went up to 20 A/cm^2 , also with good results.

The second part of the project was to build cathodes that reproduced the Chinese cathode morphology, composition, chemistry and electrical behavior. This was done by analyzing the properties of the cathodes from China and replicating them as closely as possible. A number of these cathodes were built into close-spaced diodes and tested. The results were inconclusive. One positive result, however, was that we learned how to make submicron tungsten and nanometer-sized scandia from materials on hand.

Altogether six diode testers were built with four cathodes in each, for a total of 24 cathodes. About 6,000 hours of life has been accumulated on some of these cathodes. Three open-structure devices were built also, with one cathode in each.

A third element in the project was to conduct a theoretical investigation of the scandate cathode and propose a mechanism for its operation. This was carried out by Professor Ivor Brodie and his student Arthur Carpenter at U.C. Davis. It included an analysis of data on both Chinese and e beam scandate cathodes and SEM analysis of cathode microstructures.

1.0 PROJECT OBJECTIVES

The project had six technical objectives:

- 1) Procure and study scandate cathodes from BJUT in Beijing.
- 2) Emission test these cathodes in both close-spaced diode and open-structure formats.
- 3) Develop a theoretical model of emission mechanisms for the scandate cathodes. The theoretical model must explain the known properties of scandate cathodes:
 - a) extremely low work function
 - b) extremely diffuse transition from temperature-limited to space-charge-limited flow. Is this due to patch effect, i.e., variation in work function spatially, or is it due to some non-linear mechanism for emission such as semiconductor effects? Why is this transition different from other cathodes?

- c) The fact that the cathode is able to produce high current density with scandium oxide on the surface, which is an insulator.
 - d) Why traditional scandate cathodes were irreparably damaged by ion backstreaming, but the BJUT cathodes seem to repair themselves after 30 to 120 minutes' operation at 1100° CB.
 - e) Why nanoparticle scandia seems to produce better emission than previous scandate cathodes that did not use nanoparticles.
 - f) Why operating the new scandate cathodes at high temperature seems to improve their performance.
 - g) If scandia is immobile and highly refractory, as claimed, the model must explain how it gets to the surface of the cathode and is diffused uniformly across the surface, based on SEM and Auger studies.
- 4) Acquire or produce material and develop processes to fabricate scandate cathodes similar to those from China.
 - 5) Produce new cathodes similar in structure and performance to the Chinese cathodes.
 - 6) Emission test the new cathodes in close-spaced diodes and open-structure testers, analyze the data, and propose improvements.

2.0 WORK PERFORMED

The work consisted of evaluation of Chinese cathodes, construction of e beam cathodes, construction of test vehicles, SEM studies of cathode microstructure, design and construction of pierce open structure testers, theoretical studies, materials fabrication, cathode fabrication, and emission testing of cathodes on diode and open structure format.

2.1 Testers

Table 2-1 gives serial numbers and data in each test vehicle constructed. There were 11 such vehicles. Three of them, SNA0102, A0103, and A0110 were pierce open structure testers. Two of these contained BJUT cathodes. The first of these employed a standard e beam mixed matrix cathode to test out the device electrical and mechanical properties. There were seven close-spaced diode testers with four cathodes in each one.

2.1.1 Pierce Gun Open Structure Tester

This device is shown in Figure 2-1. It was designed and built at e beam specifically to test our standard 80-mil cathode. It allows much higher loadings than close-spaced diodes and does not suffer from the other drawbacks of diodes, such as barium recycling, plasma formation, arcing, trapping of contaminants, etc.

The device can be made cheaply because it uses a glass-rod structure with welded stainless steel standard parts everywhere except the second collector, which is made of molybdenum.



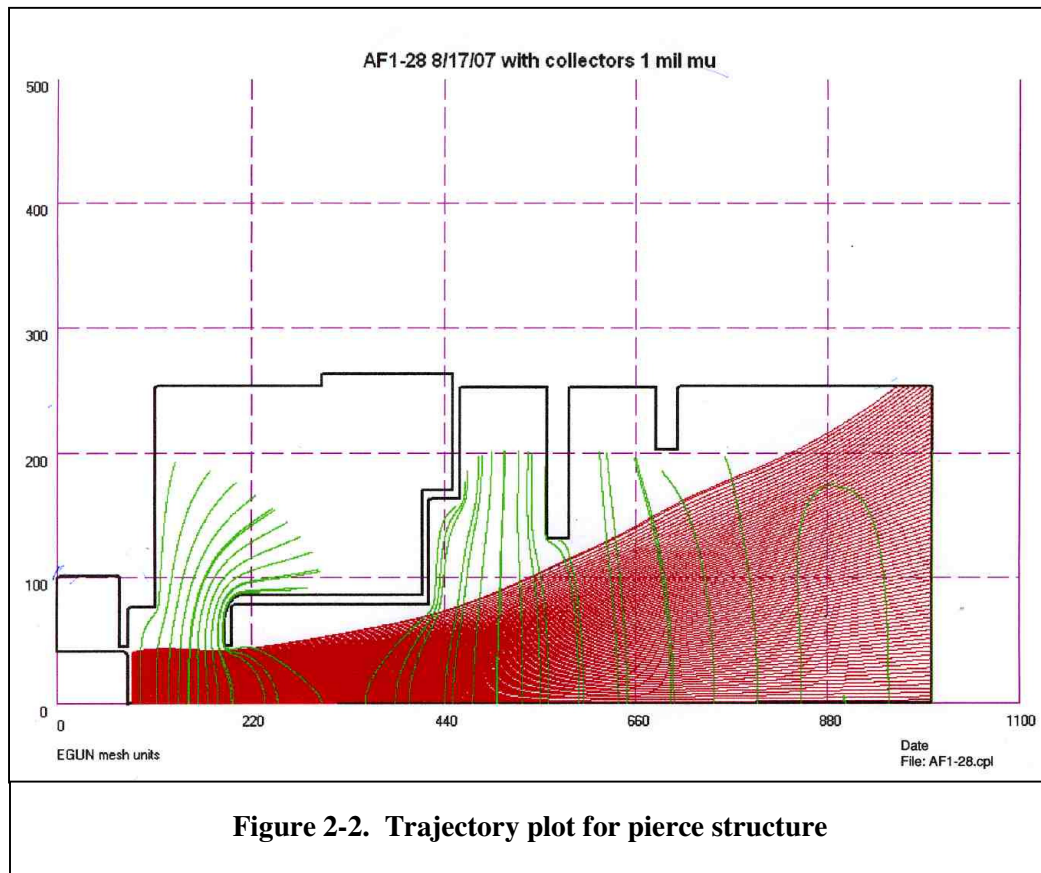
Figure 2-1. Pierce Gun Open Structure Tester

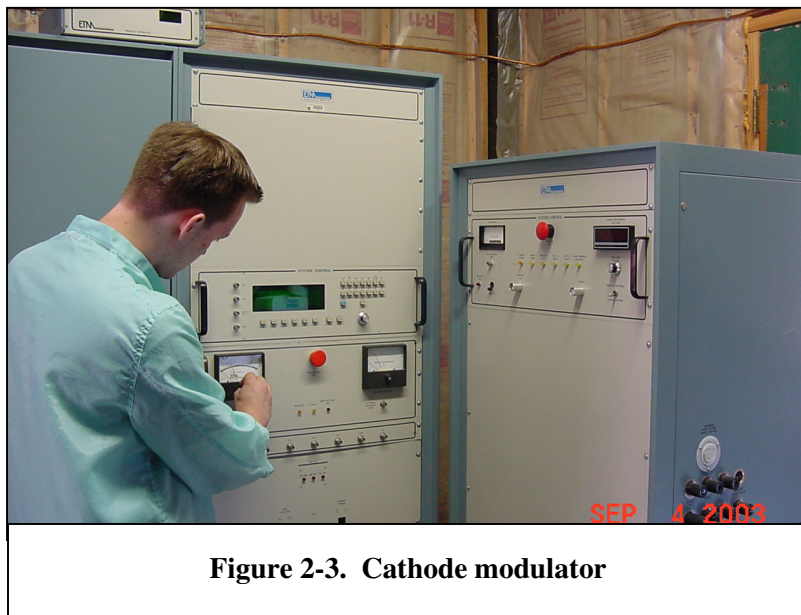
Also lowering its cost is the glass vacuum envelope and the ability to use flashed getters for vacuum maintenance.

The device is capable of standing off 30,000 volts between focus electrode and anode, which will produce over 100 A/cm² of loading from a cathode operating in the Schottky emission regime, i.e., $j \cong j_0 e^{\frac{44\sqrt{E_s}}{T}}$ where E_s is the field strength at the surface of the cathode in volts per meter and j_0 is zero field emission current density.

The device has two collectors in addition to the anode. These can be depressed to minimize power dissipation. The second collector can be depressed to under 3,000 volts according to modeling results, without significant backstreaming of secondaries.

The basic trajectory plot for the pierce structure is shown in Figure 2-2. The cathode modulator for testing the pierce tester is shown in Figure 2-3.





2.2 Processes for Introducing Scandium Oxide into Tungsten Matrices

Table 2-1 shows properties of each of the cathode matrices used in the course of the project.

The three methods for introducing scandium oxide into our tungsten matrices are discussed below. In every case we used submicron tungsten, and approximately 50 nanometer scandia particles. We perfected a way to make submicron tungsten. Toward the end of the project we developed a method for precipitating nanometer scandia particles from a solution. Before this, we were using commercially obtained nanometer scandia. The ability to precipitate nanometer scandia from solution is crucial, because the best cathodes reported by the Chinese co-precipitate both tungsten and scandia and possibly rhenium from liquid solutions. They precipitate into a gel to prevent transport of scandia to nucleation sites and to prevent agglomeration. The basic processes we developed are listed below.

Process 1

Creation of submicron tungsten powder from 4-micron standard tungsten powder. This was done by oxidizing 4-micron tungsten in an air oven, then ball milling or mortaring the fragile tungsten oxide particles until they are reduced to particles that are under one micron. The particles were then reduced in dry hydrogen back to metal.

Process 2

Mechanically mixing nanometer scandia with submicron tungsten. This involves using a mortar and pestle to mix and grind scandia with the submicron tungsten oxide. This is fired in dry hydrogen to convert tungsten oxide to metal. The mixture is then pressed and sintered into cathode matrices. However, the small tungsten particles lead to a problem of densification during sintering that was not completely solved during the course of the project. This agrees with the Chinese in that it involves introducing scandia before matrices are pressed and sintered.

However, it probably does not distribute scandia as evenly or bring it as intimately in contact with the tungsten as the so-called liquid-liquid doping described in the Chinese articles.

Process 3

Schroff method. This is based on Schroff's patent from the 1990's. The nanometer scandia was suspended in lecithin, which is a powerful dispersant. This prevents agglomeration of scandia particles. Then we simply dipped tungsten cathode matrices into this suspension. Because the scandia particles are much smaller than the pores in the tungsten, they should be carried into the matrix interior. Then the matrices are dried and redipped, etc., until a build-up of about 3% by weight occurs. The tungsten matrices were made from submicron tungsten powder made in Process 1. After drying, the cathodes are impregnated.

Process 4

Introduction of rhenium. Rhenium is supposed to cause the tungsten to form spherical particles that are .6 to .8 microns in size. Tungsten oxide, rhenium oxide and scandia, all nanoparticles, were mixed in an aqueous solution with lecithin dispersant. The mixture was then dried and fired at 1,000° C in dry hydrogen. The tungsten-rhenium particles grow into grains .6 to .8 microns in size, with nanometer scandia clinging to them. They are then pressed and sintered into cathode matrices. A more advanced process is to dissolve tungsten oxide, rhenium oxide, and scandia, then precipitate out. Tungsten comes out as .6 to .8 micron blocks. Scandia comes out as nanoparticles clinging to tungsten. We did not attempt this process.

Process 5

Formation of nanometer scandia. Scandium nitrate is dissolved in pure alcohol. Then oxalic acid is added and nanoparticles of scandia precipitate out. We were successful with this process.

2.3 Experimental Method

Measurement of cathode performance was carried out by varying the anode voltage and varying the cathode temperature as is standard for the characterization of cathodes.

The cathodes were mounted in the standard e beam closed spaced diode configuration. The nominal cathode diameter was 2mm with a cathode-anode spacing of 0.5mm shown in Figure 2-4. A resistive heater element is placed behind the cathode and a small hole in the center of the anode allowed the surface of the cathode to be viewed. The cathodes were pulsed at a frequency of 1 KHz with pulse duration 30 microseconds.

Characterization data was collected by setting the cathode temperature and measuring the anode current while varying the voltage on the anode. The cathodes were set to their highest temperature, allowed to stabilize, and then the temperature was incrementally reduced. Sufficient time for

temperature stabilization and the short duty cycle of the cathodes kept the temperature stable through each test cycle.

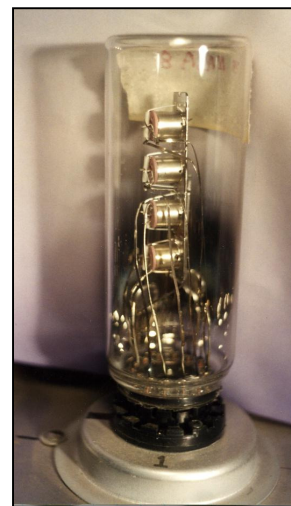


Figure 2-4. Diode tester

Temperature measurements were made using a micro-optical pyrometer (disappearing filament type) by Pyrometer Instrument Company. The pyrometer readings were related to the power dissipated in the cathode heater by a least squares reduction. The conversion from brightness temperature to true temperature was made using an emissivity constant of 45% at 600nm for tungsten. Calibration of the pyrometer was made by melting a eutectic (copper/silver) and an alloy (copper/gold) in a hole that was more than 5 times as deep as it is wide, so as to emulate a true black body source. This procedure was carried out in a carbon rod heated in a hydrogen furnace through a quartz window.

In order to find a relation between temperature and heater power, data was collected for 10 different power set points. The measured cathode temperature was then converted to brightness temperature using an emissivity constant of 0.45 for tungsten observed at 600nm and a least squares reduction was used to fit the data to a simpler power function. This power function allowed for temperatures to be extrapolated between the original data and automated data. Collection could take place with heater power being recorded, not temperature.

The zero field current density J_0 was determined by fitting straight lines to the temperature limited part and the space charge limited part of the I-V curve. The intersection of the two lines marked the zero field current density for that temperature. Richardson plots and I vs. V plots were obtained using this data. The work function ϕ and the Richardson constant A were then calculated from the plots. Another method to determine the zero field current density uses a 10% deviation from the $V^{(3/2)}$ power law for space-charge limited flow. When the current drops 10% from the expected value the cathode is assumed to be shifting over to temperature limited flow. This method has been used by Gartner¹ and is useful with scandate cathodes that do not exhibit sharp transmissions from space-charge limited to temperature limited flow, see Appendix A.

Table 2-1

#	Cathode 1	Cathode 2	Cathode 3	Cathode 4
A0101 1/20/08	Pellet lot 091307-1 #6, M80 Semicon impregnant, 40/40/20 4uW/Os/raisin mix 022706-1 Roller milled 4 hours extra 12/5/07. pressure 290 sinter 1650/5min Life test started 10/29/07 Knee 1000 at 9 days Knee 960 at 47 days	Pellet lot Dis(china)#6 0.080" diameter Old Chinese Cathode Semicon impregnant 72% Dense nano particle Scandate, sub micron W SN:E333-0	Pellet lot Dis(China) #7 0.080"diameter Old Chinese Cathode Semicon impregnant 72% Dense nano particle Scandate, sub micron W SN: E346-8	Pellet lot 091806 #8 M80 2-Layer cathode E-beam Scandate Semicon impregnant Top: Scandate 2% mix Raisin 50/30/20% Os/4uW/Rasin Bottom: 50/50% RaisinW/Os
A0102	Pierce tester M80 E-beam Raisin 40/40/20 4uW			
A0103	Pierce Tester Chinese			
A0104 2/5/08	Pellet lot 112107-1 #3 M80 2-Layer Nano- Scandate Top: Sub micron W 3.6% nanomite Sc2O3 Density 77% Bottom: 100% 4uW Density 55.3% Sinter 2000C 5min Pressure 270 lbs. Mix# 112007 Mechanical Mixing	Pellet lot 071705 #4 Older Chinese Scandate From 2005 for Resivour .080" diameter Semicon impregnant 78% dense Date: 7/17/05	Pellet lot 071705 #5 Older Chinese Scandate From 2005 .080" diameter Semicon impregnant 78% dense Date: 7/17/05	Pellet lot SDMI 0710-5 New Chinese Scandate 0.080" Submicron W Nano- Scandate Impregnated in china Patted heater Activated at excessive temperature: failed
A0105 1/7/08	Pellet lot 112107-1 #2 M80 2-Layer Nano-Partic Scandate Top: Sub micron W 3.6% nanomite Sc2O3 Density 77.1% Bottom: 100% 4uW Density 55.3% Sinter 2000C 5min Pressure 270 lbs. Mix #112007 Mechanical Mixing	Pellet lot 112107-1 #5 M80 2-Layer Nanoparticle Scandate Top: Sub micron W 3.6% nanomite Sc2O3 Density 77.1% Bottom: 100% 4uW Density 55.3% Sinter 2000C 5min Pressure 270 lbs. Mix #112007 Mechanical Mixing	Pellet lot 121207-1 #5, M80 Semicon impregnant, 40/40/20 W/Os/raisin, powder mix 022706-1 4uW Pressure 330 lbs. Sinter 1650 5min Ball milled 4 hours on 12/5/07 Life test start 1/7/08 No knee at 0 hour Respectable knee 970C at 14 day	Pellet lot 120607-1 #10, M80 Semicon impregnant 65/35 W/Os, 4uW powder mix 120507-1 rod milled 2 Hr. Density 59% Pressure 290, sinter 1650/5min. Life test start 1/7/08 Knee 1060 at 0 hour Good Knee 980 at 33 days (800Hr)

A0106 1/27/08	Pellet lot 100206-1 #12 M60 612 impregnant, 67% density 40/40/20 W/Os/raisins Pressed 240 lbs. life test start 1/27/08 Broad knee above 1050 at 7 days	Pellet lot 022702-1 #8, M80 Semicon impregnant 65/35 W/Os pressure 200, Density 66.7% 1650 C/5min. Life test started 1/26/08 Knee 1030 at 4 days, poor shelf powder unknown,	Pellet Lot 0710 #3 0.080" Chinese Scandate Impregnated in China Potted heater Sub micron W Nano meter scandate knee at 850C at 700 hours at 20A/sq.cm SDMI 0710-3 323.2	Pellet Lot 0710 #4 0.080" Chinese Scandate Impregnated in China Potted heater Sub micron W Nano meter scandate (best emission) knee 820 at 984 hours At 20A/sq.cm SDMI 0710-4 323.2
A0107	Pellet lot 120607-1 #5 M80 Semicon impregnant 65/35 W/Os roller milled 2 hours powder mix 120507-1 4u W Pressure 290lbs. 1650 C 5min. density 57.4 Life test began 2/6/08 Knee 1000C 600hours 6 A/sq.cm	Pellet lot 010808-1 #3 M80 Scandate 612 impregnant Sol-Gel W/Re/Sc Submicron W, nano meter scandia Density 76% Pressure 284 lbs. 2000C 5min. Mix 121807 No Knee, density too high	Pellet lot 112107-1 #6 M80 2-Layer Nano-Partic Scandate Top: Sub micron W 3.6% nanomite Sc2O3 Density 77% Bottom: 100% 4uW Density 55.3% Sinter 2000C 5min Pressure 270 lbs. Mix #112007 Mechanical Mixing No knee.	Pellet lot 121207-1 #2, M80 impregnated, powder 022706-1 40/40/20 W/Os/raisin 4uW, roller milled, sinter 1650/5min. pressure 330lbs. mix 022706-1 Knee 1000C at 620 hours 6 A/sq.cm
A0108	Pellet lot 010808-1 #5 M80 Scandate 612 impregnant Sol-Gel W/Re/Sc Submicron W, nano meter scandia Density 76% Pressure 284 lbs. 2000C 5min. Mix 121807 Died 2 days	Pellet lot 011608-1 #2 M80 Scandate 612 impregnant Sol- W/Re/Sc Submicron W, nano meter scandia Density 69% Pressure 290lbs. 1750 10 min Mix121807	Pellet lot 011608-1 #7 M80 Scandate 612 impregnant Sol- W/Re/Sc Submicron W, nano meter scandia Density 69% Pressure 290lbs. 1750 10 min Mix121807M80 Shorted heater	Pellet lot 011608 #8 M80 Scandate 612 impregnant Sol- W/Re/Sc Submicron W, nano meter scandia Density 80% Pressure 290lbs. 1750 10 min Mix121807M80
A0109	Pellet lot 030408-1 #11 M80 Scandate 4uW Density 64% Sinter 1650C 5 min. Pressed 300lbs.	Pellet lot 041408-1 #10 M80 Scandate Sub micronW 3.5% nanomite Sc2O3 Pressure 220 Sinter 1750 3 min.	Pellet lot 041408-1 #13 M80 Scandate Sub micronW 3.5% nanomite Sc2O3 Pressure 220 Sinter 1750 3 min.	Pellet lot 041408 #14 M80 Scandate Sub micronW 3.5% nanomite Sc2O3 Pressure 220 Sinter 1750 3 min.
A0110	Pellet lot # M80	Pellet lot # M80	Pellet lot # M80	Pellet lot # M80

3.0 RESULTS OBTAINED AND DEVELOPED THEORY

3.1 The Chemistry of Scandium Oxide

Since the addition of scandium oxide has resulted in significant improvement in cathode performance it was of interest to see in what chemical reactions it may be involved. The important parameters for the principal oxides involved are shown in Table 3-1 below.

Table 3-1

Substance	Melting point °C	Heat of formation kJ/mol	Density gm/cc
BaO	1923	-548	5.72
Al ₂ O ₃	2045	-1675	3.97
Sc ₂ O ₃	2485	-1906 ³	3.86
WO ₃	1473	-831	7.16
CaO	2580	-635	3.3

During the impregnation of the porous tungsten matrix the eutectic of 3.7BaO.Al₂O₃ is formed at about 1700 °C and the temperature usually does not exceed 2000°C. There is no evidence that scandium oxide forms a low temperature eutectic with BaO, hence it does not melt but, if included in the impregnant mixture, particles of scandium oxide may be carried into the pores by the other liquid components. Since the pores are of the order of one micron or less, larger particles will be filtered out and only nanoparticles will be carried in. Because of its high heat of formation scandium oxide will not form free scandium metal by reaction with the tungsten matrix. The same is true for aluminum oxide and in fact free aluminum has never been identified in this type of cathode. Since the scandium oxide never liquefies it is unlikely that it is doped with barium as the large barium atom (diameter 4.48 Ang) is unlikely to be able to diffuse into the scandium oxide lattice. It is well known that aluminum oxide becomes loosely bonded to barium oxide during impregnation forming BaO.Al₂O₃ and 3BaO.Al₂O₃. However, it is unlikely that the corresponding scandium compounds are formed, because of the much higher heat of formation of scandium oxide and because the BaO and Sc₂O₃ molecules are never intimately mixed in the molten phase. Note WO₃ is formed when BaO reacts with tungsten to form free barium but it is always tied up with barium oxide as a barium tungstate (BaO.WO₃ or 3BaO.WO₃).

Thus it appears that scandium oxide probably remains in the form of pure nanoparticles throughout the processing and life of the scandate cathode whether it is incorporated in the impregnant or the tungsten matrix or deposited on the surface.

3.2 Process for Producing Nanoparticles of Scandium Oxide

3.2.1 Sol-Gel Processes

In the “sol-gel” process, a uniformly distributed colloidal suspension of non-agglomerated nanoparticles in a liquid is formed (often called a “sol”). The carrier liquid may be highly insulating as are many organic solvents. In this case the particles are often charged and are held apart by mutual repulsion. Water colloids are more common but its conductivity is relatively high and particles are held apart by a surrounding di-pole layer of ions and counter ions. To create a sol the suspended particles are typically of the order of 30 to 100 nm in size and may or may not be charged. Polymeric materials are often added to the sol so that as the carrier liquid is removed by evaporation a quasi solid “gel” is formed that keeps the particles uniformly distributed and prevents agglomeration during drying. Finally as the carrier liquid is removed entirely and the gelling material is burned off leaving an intimately mixed layer of particles that may be further sintered to form a solid.

For incorporation in the tungsten matrix BUT² used a sol gel process to create a uniform distribution of nano sized scandium oxide and tungsten particles inside the pores of a porous tungsten matrix. The details of this process are not given other than to say it is a liquid –liquid (L-L) process. The scandium oxide doped porous matrix is subsequently impregnated in the molten phase with 4:1:1 barium calcium aluminates to form the cathode. Important for the operation of the cathode the impregnant and scandium oxide particles are removed from the cathode surface by using water to a depth of several microns². In operation nano particles of scandium oxide migrate to the surface by an as yet undetermined process along with the free barium.

Recently Grosso and Sermon⁴ have published a detailed but time-consuming process for making a scandium oxide sol (particle size 66x37x4.5nm) in an alcohol medium.

3.2.2 Precipitation Process

Xiu et al⁵ at Shenyang, China have precipitated scandium oxide nanoparticles (43.5nm) from scandium nitrate dissolved in pure alcohol using oxalic acid dehydrate as the precipitant. E-beam has successfully used this process to produce a suspension of scandium oxide nanoparticles and impregnate a porous tungsten matrix with 4% by weight scandium oxide. SEM pictures (Appendix B Images 3 and 4) show clearly the deposition of nano- particles on the interior walls and surface of the porous tungsten matrix.

3.2.3 Laser Ablation Process

In the LAD process a nano-crystalline top layer 100 – 500 nano-meters thick is deposited on the filled pores of a standard 4:1:1 impregnated cathode¹. It is possible that some free scandium is released during the LAD process as some tungsten is incorporated in the target. However the vapor pressure of scandium is high enough (about 10^{-5} torr at 1000°C) that it would be all lost during cathode activation. In operation barium generated in the impregnated porous tungsten substrate diffuses through the scandium oxide nano-layer to activate the cathode.

3.3 Data Results

Measurements were made on the following cathode types:

1. Chinese scandate cathodes supplied by Prof. Yiman Wang (designated YS)
2. A first attempt by e beam, inc. to repeat the Chinese process (designated YE)
3. Standard 4:1:1 impregnated cathode supplied by e beam (designated IE)
4. Standard “M” cathodes (65% W 35% Os) supplied by e beam (designated ME)

Measurements reported in the literature:

1. Top layer scandate cathodes deposited by LAD¹ (designated LAD)
2. Chinese scandate cathodes² (designated YC)

The emission at zero field, $J \text{ A/cm}^2$ at a given temperature $T^\circ\text{C}$ (true) for these cathodes is given in Figure 3-1.

The emission at zero field $J \text{ A/cm}^2$ at a given temperature T Kelvin was also fitted to the Richardson equation ($J_0 = AT^2 \exp(-\phi_e/kT)$) at the mid temperature point yielding the results given in Table 3-2. Note that ϕ and A values are sensitive to the method by which J the emission at zero field is measured. The measurements taken at e beam were consistent but the measurements quoted from the literature may not be exactly similar.

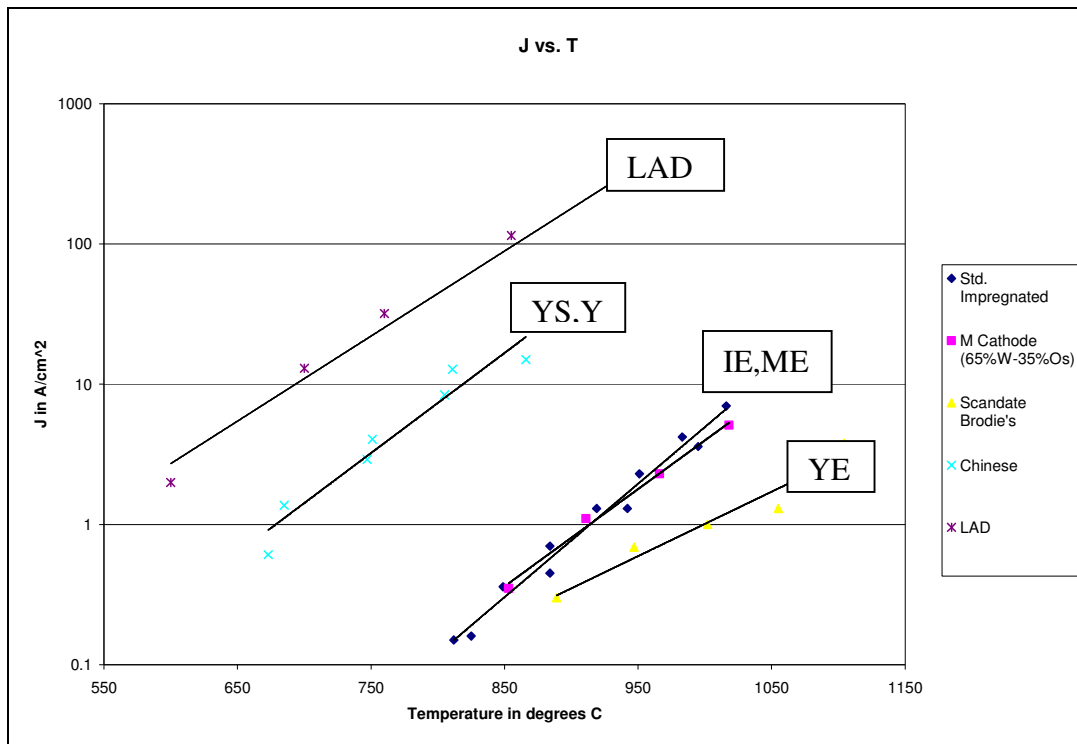


Figure 3-1

Table 3-2

Cathode type	Work function ϕ eV	Richardson A constant $Amps/cm^2 \cdot K^2$
LAD	1.15	8
YS	1.2	6
YC	1.1 – 1.2	6 - 7
IE	1.61	11
ME	1.61	11
YE	1.15	0.022

The above results confirm that the scandate cathode is capable of giving emission at a given temperature over two orders of magnitude greater than that of standard I cathodes and M cathodes at least in 30 microsecond pulses repeated 1000 times per second. The mission strongly

depends on the quantity of scandium nanoparticles present. Much work has yet to be done on optimizing conditions for continuous operation at the highest current densities.

Pierce Gun Configurations of the Chinese cathode (YS) were tested to determine and gain a better understanding of

3.4 Physics of Electron Emission from Barium Activated Scandium Oxide

The physical attributes of scandate cathodes as indicated in references 1 and 2 and this report may be summarized as follows:

1. The crystallites of scandium oxide are in a range 10 – 500nm
2. The work function is in a range 1.15 – 1.2eV
3. The Richardson “A” value is in a range of 6 – 8 amps.cm⁻².K⁻²
4. In the saturated region of the current –voltage characteristic, logJ is proportional to Vⁿ where n lies between 1/2 and 3/2 and n increases with increasing temperature
5. Emission “poisoning” by ion bombardment is irreversible or at best very slow to recover
6. Nanoparticles of tungsten may have to be present for emission to be stable

Any model used to emulate the mechanism of the cathode should quantitatively account for these attributes. To this end two prior models have been reviewed in detail. The first is based on the concept that scandium oxide semiconductor can be doped with barium to donate electrons to the conduction band as has been proposed for the barium oxide cathode⁶. This seems unlikely for scandium oxide as it does not melt and barium being a large molecule is unlikely to diffuse into the semiconductor even at the temperatures involved. The second⁷ is based on the concept that electrons crossing the Schottky barrier from the metal substrate to the semiconductor can travel to the emitting surface with a mean free path for scattering less than the length of the crystal. Mean free paths for oxides are typically in a range of 1 to 10nm and, as the crystals dimensions are of the order 50nm, substantial energy loss by scattering occurs before electrons reach the vacuum interface where they now have insufficient energy to escape. Hence a new model based on the chemistry of scandium oxide discussed above is proposed, as illustrated in Figure 3-2, which appears to have the required attributes.

3.4.1 The New Proposed Model

The assumptions used are:

1. Even at the operating temperature (~ 1000K) due to the high band gap of 5.7eV (greater than that of diamond!) and surface traps for electrons, there can be very few electrons in the conduction band of the crystal and it behaves essentially an insulator.
2. The adsorbed layer of barium on the scandium oxide crystal surface forms a two dimensional plasma over the entire crystal surface enabling electrons to travel from the

tungsten substrate to the emitting surface. The complete theory for the Fermi level of a 2-D electron gas⁸ is complex and difficult to apply, however the simple zero order theory⁹, which is probably good enough for showing trends for this application, gives a Fermi energy of

$$EF = \frac{\hbar^2}{2me} \left(\frac{2N}{\pi} \right) \quad \text{equation (1)}$$

where N is the number of electrons per unit area. Scandium oxide has a cubic crystal structure¹³ with a lattice constant $a_0 = 0.9845 \text{ nm}$ (JCPDS file 5-629) Thus the number of surface lattice units $N_s = a_0^{-2} = 1.03 \times 10^{18} \text{ m}^{-2}$. Assume each molecular site area a^2 can adsorb one barium atom, then with full coverage there will be a^{-2} barium atoms/ m^2 . The mechanism of adsorption is unclear but since each barium atom is doubly ionised it will be assumed one electron is associated with the bonding of the barium to the oxide substrate one is donated to the electron cloud. Thus $N = N_s = 1.03 \times 10^{18} \text{ m}^{-2}$. Thus from equation (1), $EF = 0.99 \text{ eV}$.

3. In a previous paper¹⁰ using a model based on the uncertainty principle and the image force acting on an electron escaping from a metal atom, I developed a simple equation for estimating the work function assuming the effective mass of the conduction electron equals the electron rest mass

$$\phi = 1.841\sqrt{EF} \left[1 + \frac{1.953}{2R\sqrt{EF}} \right]^{-1} \quad \text{eV} \quad \text{equation (2)}$$

Using R for barium = 2.14 Ang. and $E_F = 0.99 \text{ eV}$ for a barium 2D plasma gives $\phi = 1.27 \text{ eV}$. compared with the measured values for a scandate cathode of 1.15 to 1.2 eV.

4. Since the electron gas is two dimensional, electrons have no energy perpendicular to the plane of the emitting surface on which it is adsorbed and hence can only escape from the edges of the adsorbed layer between adjacent crystallites as shown in Figure 3-1. The thickness of the adsorbed barium layer will be approximately the diameter of a barium atom, ~0.5nm perhaps enhanced by surface tension, thus for a square faced crystal 50 nm on a side the ratio of the emitting area to the area of the face will be ~25/ 2500 or ~1%. The ratio of the measured "A" value to the theoretical value for a metal ($120.4 \text{ Acm}^{-2}\text{K}^{-2}$) is ~6/120 or 5%. The theoretical "A" value for a 2-D Fermi gas can be estimated.
5. In the saturated region an electrical force acts on the electrons in the plane of the surface in a direction enabling them to escape thus providing a mechanism for a V^n characteristic. Given the current J (A/cm^2) at a plate voltage above that required for the current density at zero field J_0 (A/cm^2) and the temperature T (K), the electric field F (volts/cm) at the cathode surface can be estimated from the solution of Fry's¹² equation.

The relation between the saturated emission J and surface field F is thus obtained.
Experimental results from the Chinese scandate cathode indicates

$$J = J_0 e^{\frac{F}{CT}} \quad \text{equation (3)}$$

6. Ion bombardment sputtering of the cathode will tend to close the gap between crystallites thereby permanently preventing exposure of barium at the gap to the vacuum.
7. If it is confirmed that nanoparticles of tungsten have to be present, their role may be simply to help keep a space between scandium oxide particles so that free barium may more easily diffuse from the interior to maintain the surface mono-layer.

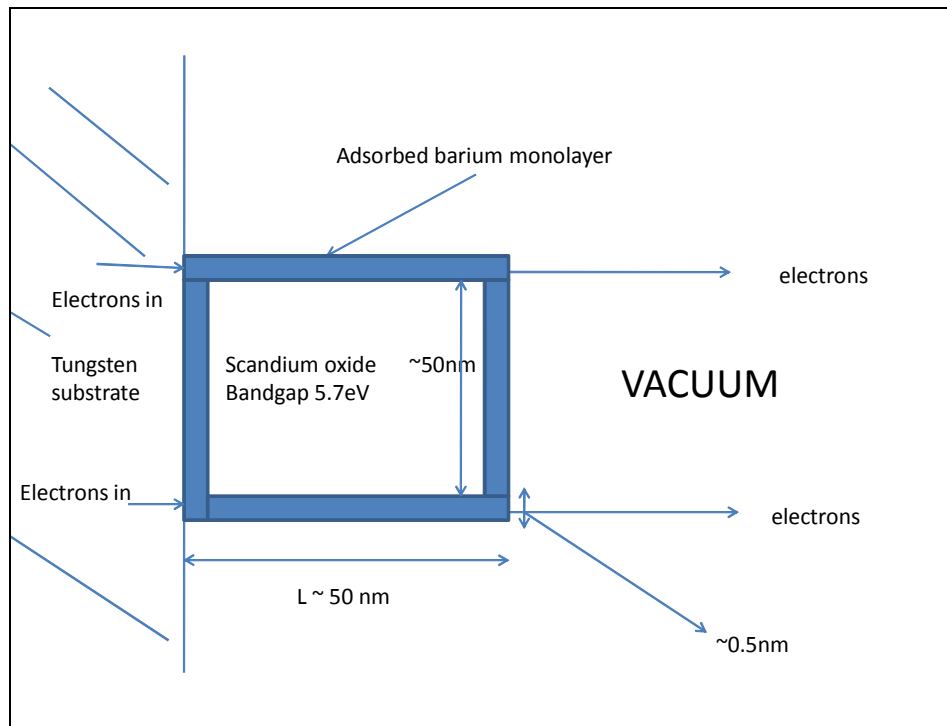


Figure 3-2

3.4.2 Future Refinements On The Proposed Model

Despite the approximations used, the proposed model has at least shown itself to be plausible. It demonstrates the reason for the scandium oxide to be in the form of nano-sized particles and is capable of quantitative application to the emission characteristics of scandate cathodes. The following refinements to the model would be attempted in future work:

1. The role of the scandium oxide in the proposed model is to provide a bond for barium adsorption and to fix the maximum number of barium atoms that can be adsorbed per m^2 .

These along with the adsorption energy of barium on scandium oxide need to be studied experimentally and theoretically using “ab initio” methods¹¹.

2. Other inert materials with differing lattice dimensions which controls N and hence ϕ need to be explored.
3. Extraction of electrons from the 2-D plane under the action of a field perpendicular to the surface in the saturation region needs to be put on a quantitative basis.
4. More exact methods need to be developed for obtaining the Fermi energy and work function and “ A ” value of the 2-D electron gas.

3.5 Summary and Conclusions of Results Obtained

The first objective of the Phase I Project was accomplished, namely to validate the excellent results on scandate cathodes attained by Prof. Yiman Wang, et al., of Beijing University of Technology (BJUT).

The second objective of reproducing these results was approached but not completed. Cathodes with too few scandium oxide nanoparticles present showed the same work function as the Chinese cathodes, but a much smaller active area. A procedure for depositing much larger quantities of scandium oxide nanoparticles in the pores was developed and proven but lack of funds did not allow for the impregnation and testing of cathodes.

A third objective of developing a theoretical model that could quantitatively predict the remarkable properties of scandate cathodes resulted in the proposal of a new model which has promising features. This model has aspects which could benefit from more extensive detailed computation.

A fourth objective of introducing a graduate engineering student to the science and art of thermionic electron sources has been accomplished.

3.6 SEM Images

In order to understand scandium's role in scandate cathodes SEM images were taken of the surface of a cathode. A FEI XL30-SFEG scanning electron microscope was used to image the surface of a cathode. This cathode was a Tungsten/Osmium mix with scandium. The surface appears to be mostly closed, see Image 1. The closed surface limits the exposure of Barium or Scandium on the surface due to their inability to diffuse from within the matrix of the cathode. This can lead to poor cathode performance even if the cathode has a very low work function.

Image 2 shows the Tungsten/Osmium matrix inside one of the open pores in the surface of the cathode. Images 3 and 4 are of an individual matrix particle with nanoparticles on its surface. These nanoparticles seem to cover the surface fairly uniformly and appear to be 40-100nm in size.

The microscope was fitted with a Back Scattered Electron Detector (BSE) and an Energy-dispersive X-ray detector (EDX). In Image 5 the surface of the cathode is viewed using the BSE detector. Lighter areas indicate higher atomic weight while darker areas indicate areas with lower atomic mass. Tungsten and Osmium both have significantly higher atomic mass than Scandium. The circled areas in Image 5 were probed using the EDX tool and Scandium was detected in these areas. The lighter areas were also probed, but no substantial amount of scandium was detected.

The regions around the pores where scandium was detected are several times larger than the pores. This implies that scandium is mobile, either a scandium oxide, free scandium, or in some other form.

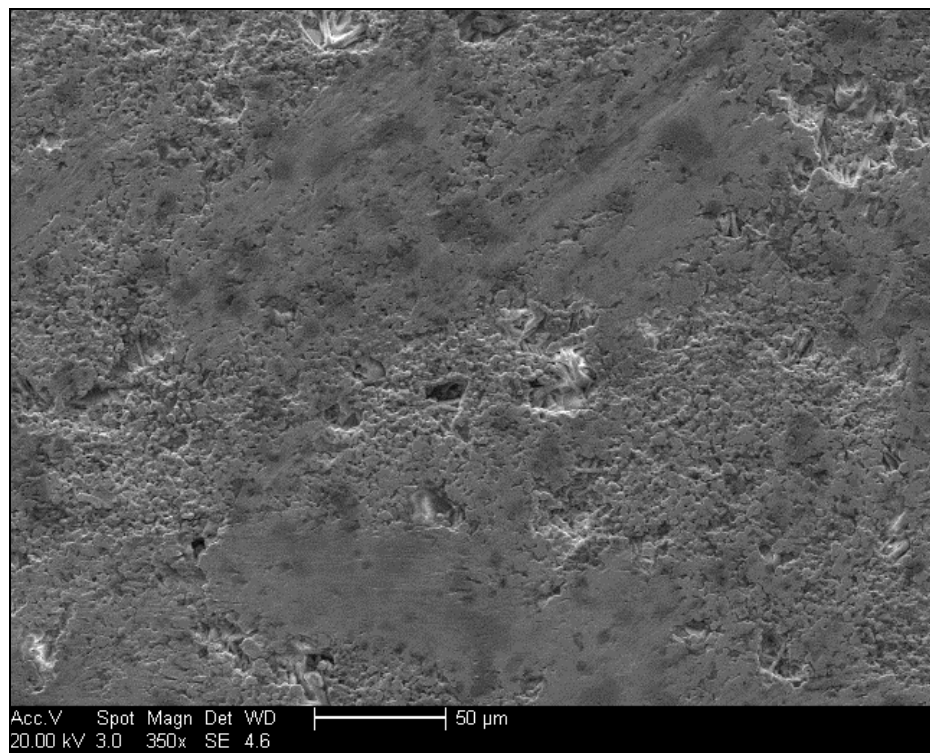


Image 1. Surface of cathode

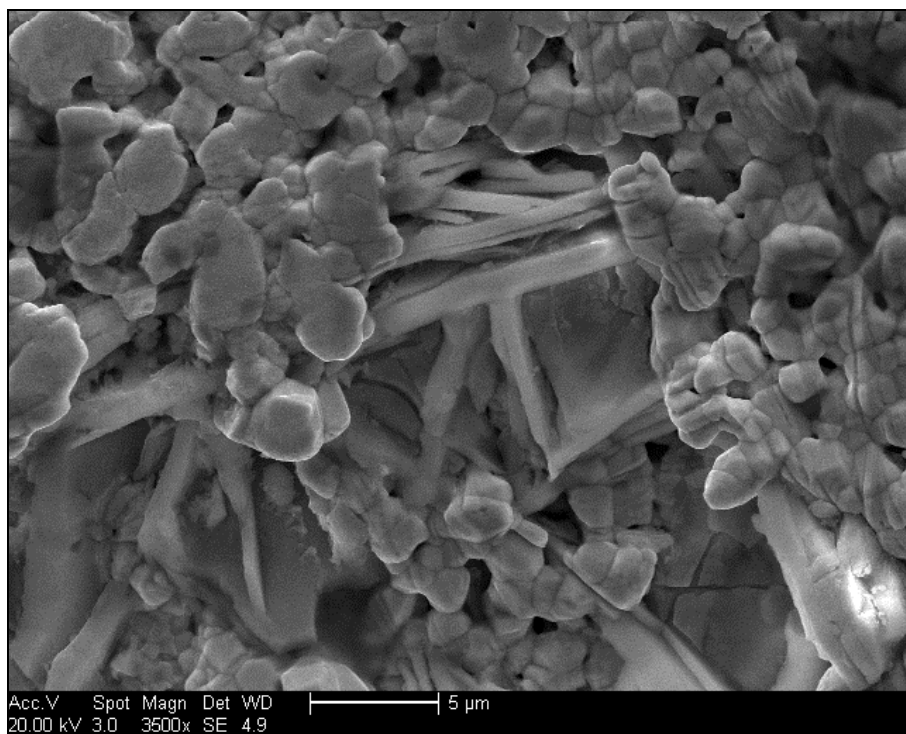


Image 2. Looking into one of the holes on the surface of the cathode

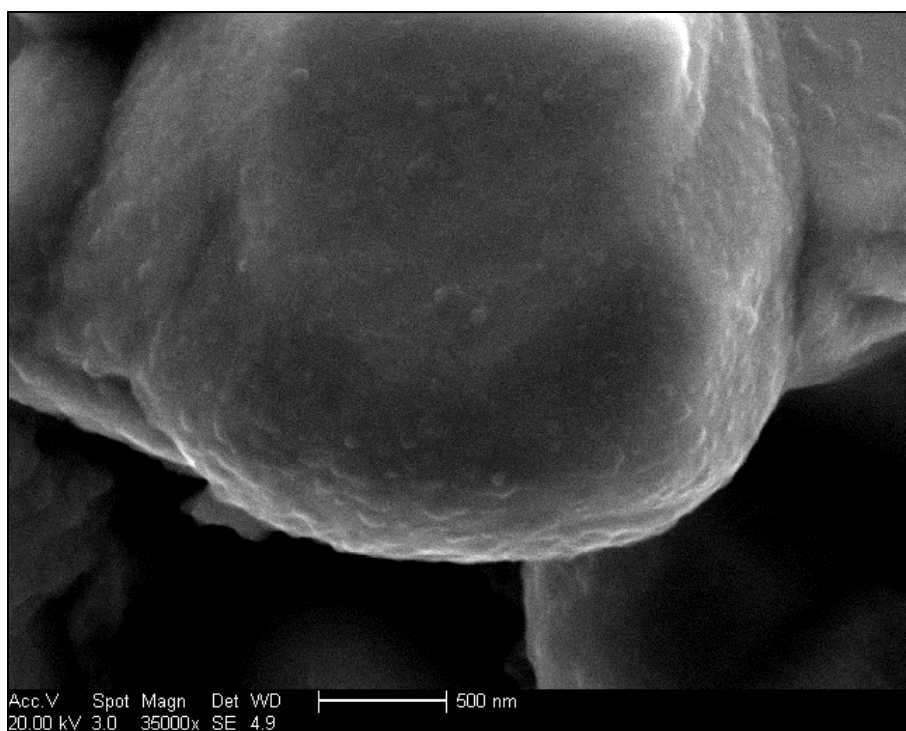


Image 3. A tungsten/osmium ball with nano scale

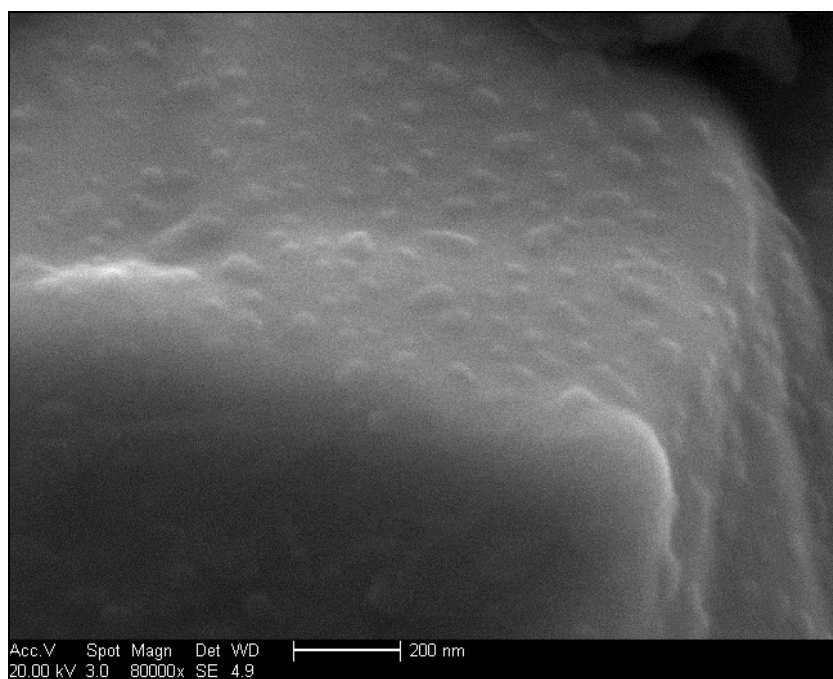


Image 4. Scandium

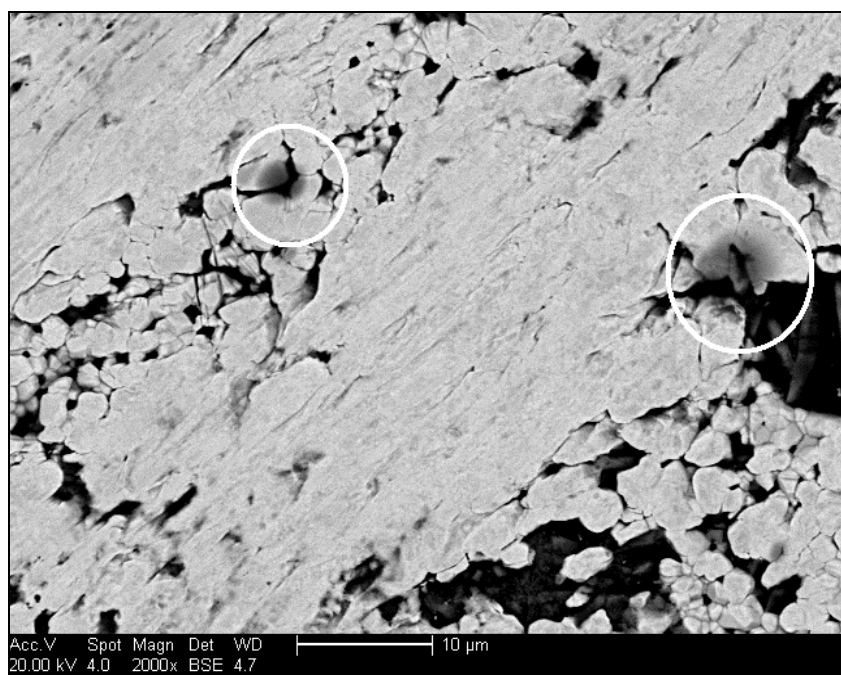
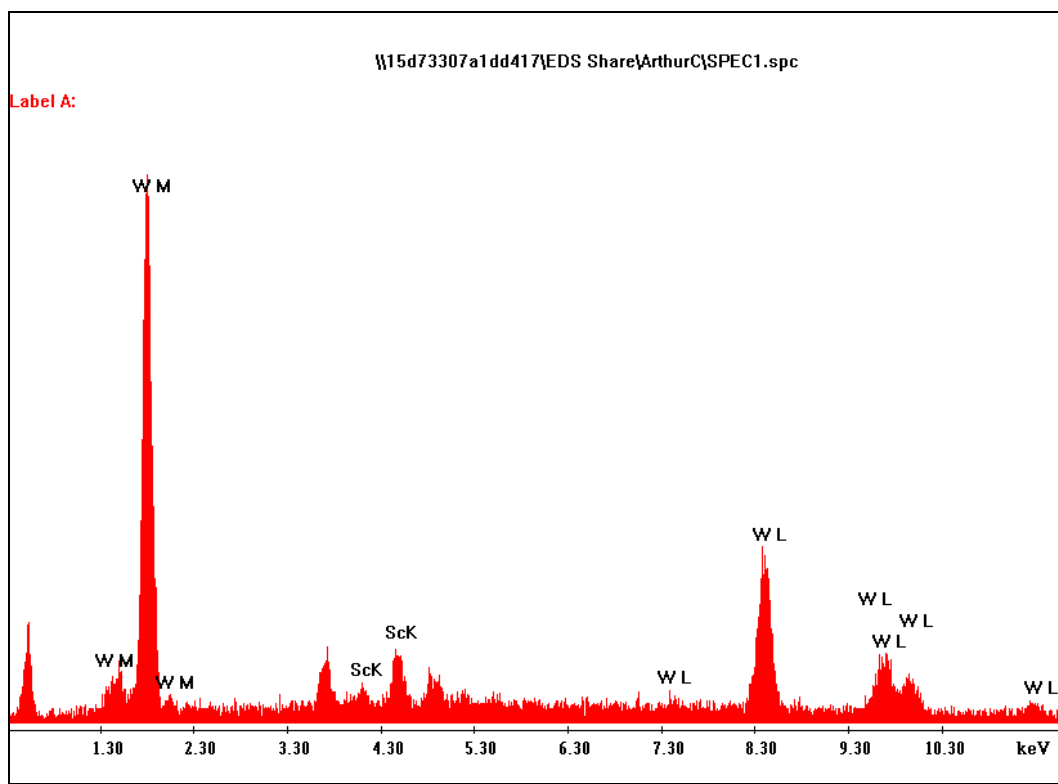


Image 5. Back scattered electrons from the surface



Spectrum 1. EDX spectrum from larger circle (right) in Image 5

4.0 ESTIMATE OF TECHNICAL FEASIBILITY

We have proven that the BJUT scandate cathodes produce published levels of emission. We proved this on both diode and open structure devices. But there are still unanswered questions, and life span of the cathodes at high emission current is still unknown.

We have tested four BJUT cathodes for about 4,000 hours. Their activity plots are compared at 0 hours and at 4,000 hours. If anything, performance has improved. These cathodes were operated at 1,000 ° C during the course of this test. It is known that performance deteriorates rapidly above 1100° C. Nevertheless, operating these cathodes at 1,000° C is a fairly aggressive test when one considers that they produce 20 A/cm² at 850°CB.

However, a 4,000 hour life test is by no means conclusive. In this regard, feasibility is still to be determined.

The deleterious effects of ion backstreaming or back-sputtering is another problem that has plagued previous scandate cathodes. Once the scandate surface layer is removed, it does not replace itself or does so very reluctantly. This question is still unanswered.

The traditional argument is that nanoparticles of scandate will allow more rapid formation of free scandium due to the higher reactivity. Free scandium at the cathode surface provides the improvement in performance. So this argument goes. According to Professor Wang, the BJUT

cathodes can be rejuvenated by operating at 1100°C for 30 minutes to two hours. Again, the claim is that the nanoparticles of scandia have provided something that previous scandate cathodes did not – namely, the ability to bring up new scandium from the substrate. The scope of our investigation did not allow us to prove this point. Therefore, to the extent that feasibility depends on resistance to ion backstreaming, the question is still open.

The remaining question of feasibility hinges on our ability to replicate the Chinese results. This question also remains open, since we were not able to reproduce the performance of the BJUT cathodes. However, we have a reasonably clear path forward and did duplicate many of the precursor processes necessary to this end. For example, we can precipitate nanoparticle scandia from solution.

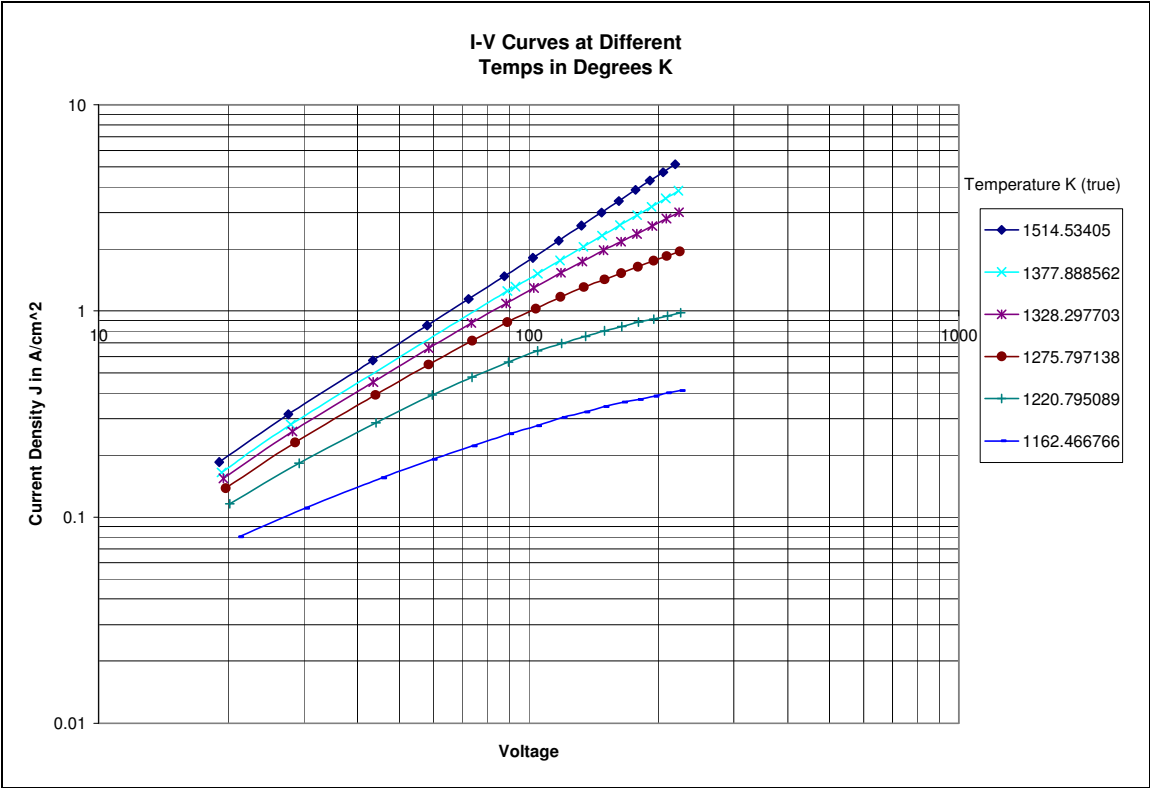
We know this cathode is feasible because we have verified its performance. Presumably, the cathode can be replicated in this country.

5.0 REFERENCES

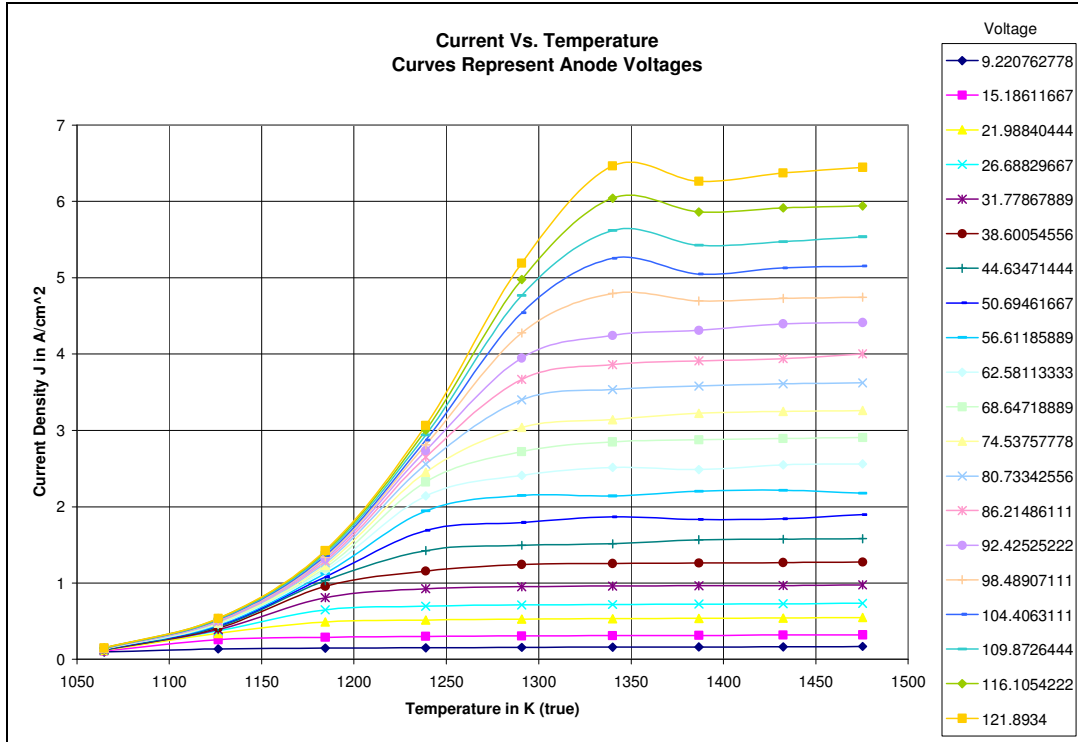
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Contacts: Georg Kresse and Jürgen Furthmüller , Institut für Materialphysik, Universität Wien, Sensengasse 8, A-1130 Vienna, Austria.
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Appendix A. Cathode Data

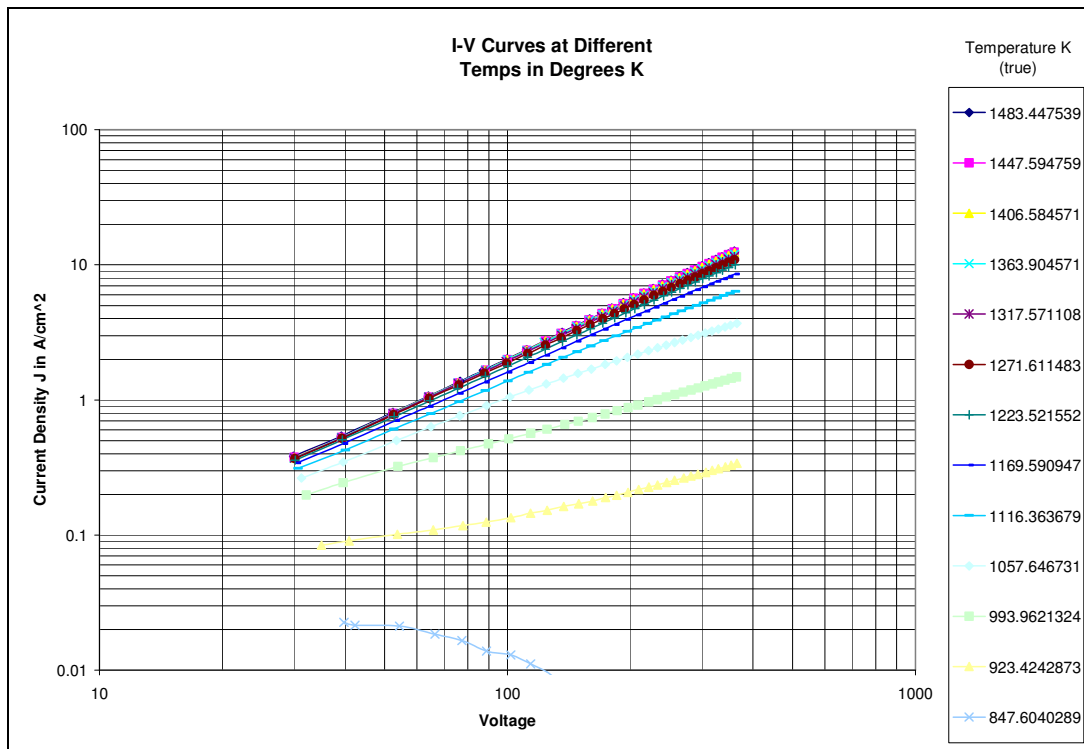
Scandate Cathode AF0105 Cathode #2

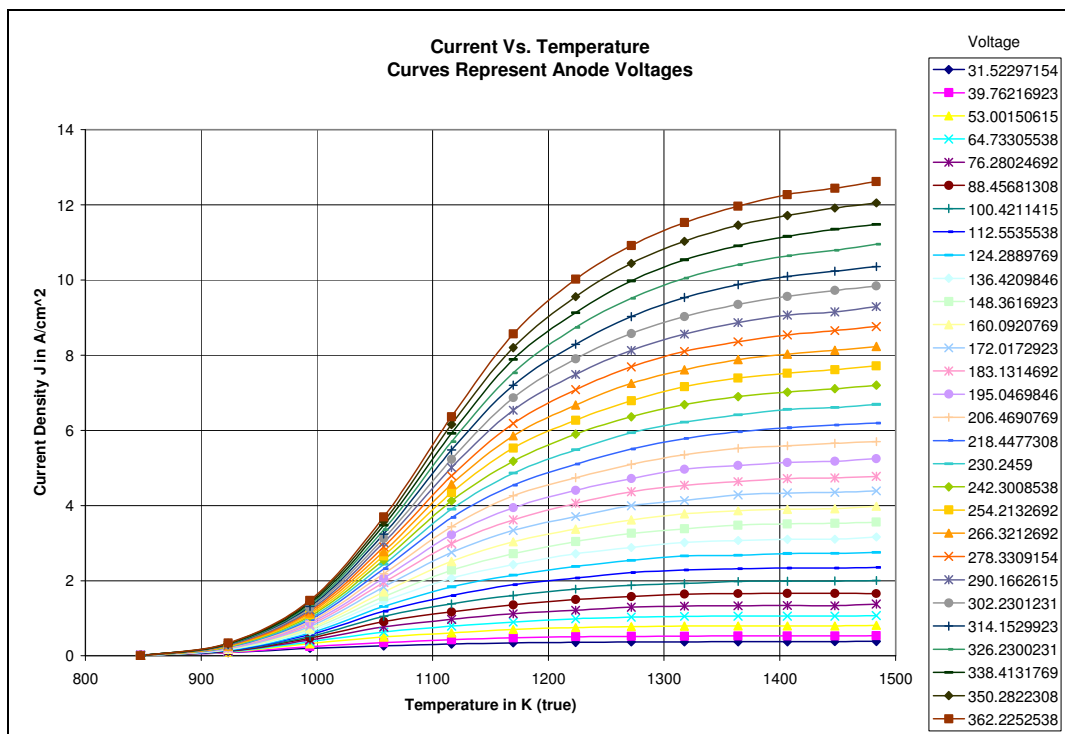


M Cathode (65%W-35%Os) AF0105 Cathode #4

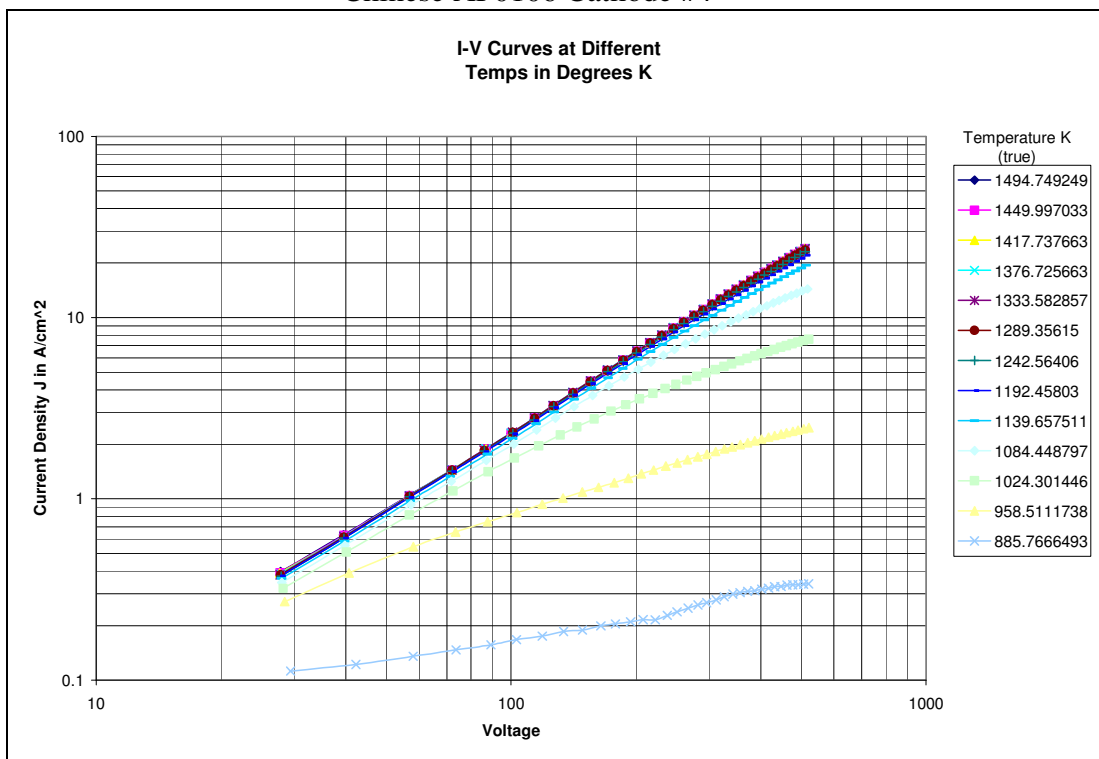


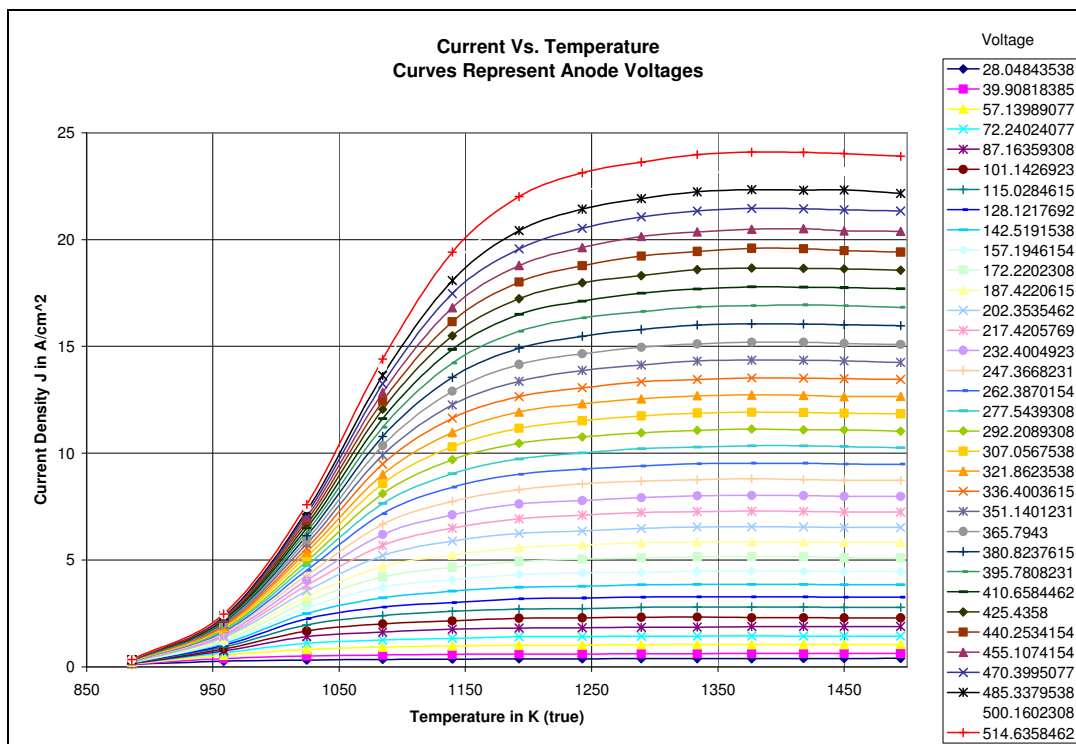
Chinese AF0106 Cathode #3



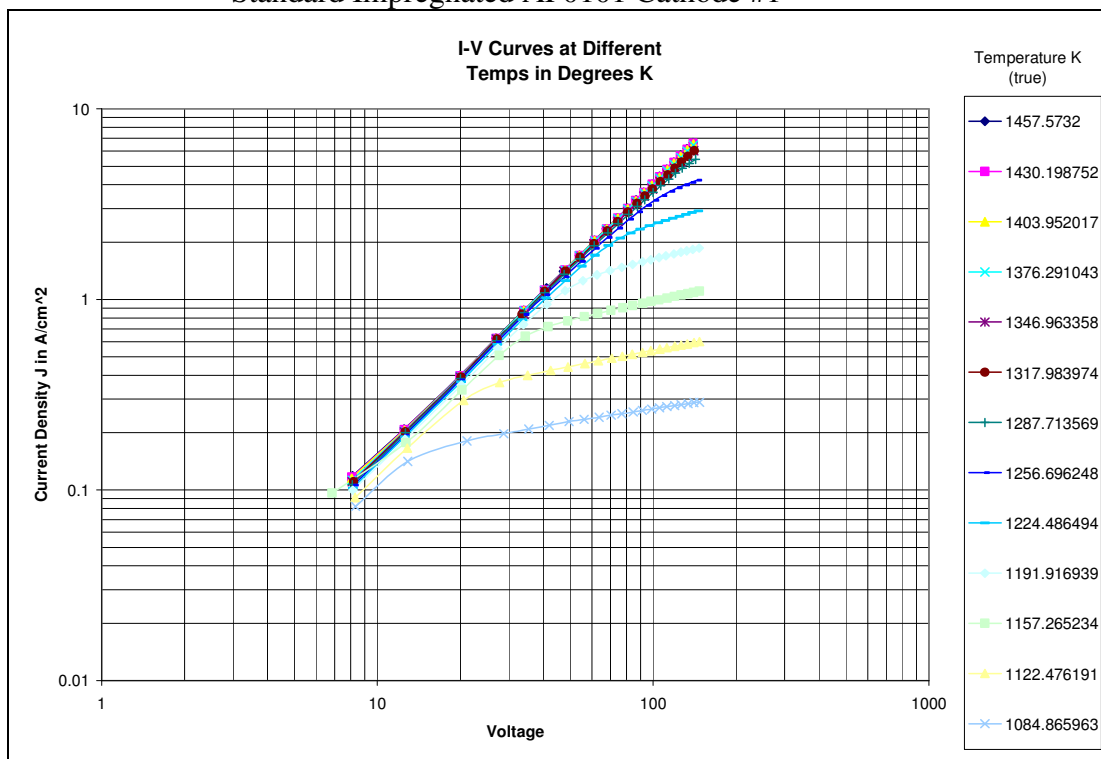


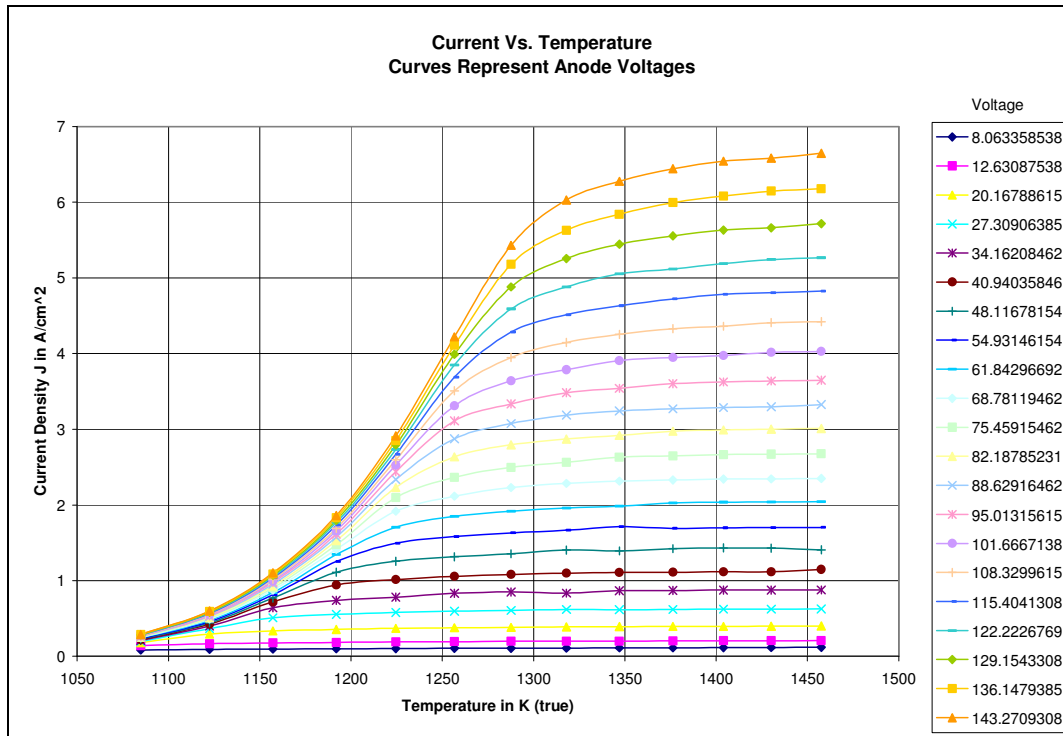
Chinese AF0106 Cathode #4





Standard Impregnated AF0101 Cathode #1





Chinese Cathode pierce gun configuration

